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(57) Abstract

A process for the branching and foaming of a polypropylene resin, being performed continuously in an extruder, comprising: (i) mixing the polypropylene resin with a peroxide selected from the group comprising the structures represented by: R_1–O–O–C(O)–C=C–C(O)–O–O–R_2, R_3–R_5–O–C(O)–O–O–C(O)–O–R_6–R_4, wherein each R_1 and R_2 represents linear or branched alkyl groups having 1–15 carbon atoms, each R_3 and R_4 represents linear or branched alkyl groups having 4–30 carbon atoms, and each R_5 and R_6 represents cyclic or linear aliphatic groups having 6 carbon atoms, (ii) heating the constituents to a temperature higher than the melting temperature of the polypropylene resin and the decomposition temperature of the peroxide while being mixed and conveyed forward, (iii) keeping the polymer melt at said temperature for a period of 3 to 100 times the half–life of the peroxide at said temperature, (iv) introducing a foaming agent, optionally also a bubble initiator, into the polymer melt inside the extruder at a position where the branching is substantially complete, (v) extruding the processed polymer melt through an extrusion die into ambient atmosphere, whereupon the polymer composition expands. The obtained polymer resins may be used in manufacturing articles by pipe extrusion, thermoforming and blow molding. Branched polypropylene resins not being subjected to foaming may be used as such in manufacturing articles by injection molding, extrusion, thermoforming, blow molding, calandering and fibre spinning.

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FOAMED POLYPROPYLENE

TECHNICAL FIELD

This invention relates to a continuous process for the chain branching and foaming of polypropylene resins, and the use thereof.

BACKGROUND AND PRIOR ART

Polypropylenes are gaining applications in existing and new market areas mainly due to their excellent cost to performance ratio. Many efforts have been made to modify polypropylene resins to give them desired properties, for instance by grafting specific compounds onto the polymer backbone, by crosslinking, and by blending with other polymers. One drawback of many polypropylene resins is their low melt strength, which is at least partly due to insufficient branching, and such polypropylenes cannot be foamed into useful low density foams.

US 5,047,485 discloses a process for the preparation of solid, gel-free polypropylene resins having increased branching and strain hardening elongational viscosity. A linear polypropylene resin in the form of a solid state fluidized bed is mixed with a peroxide and preferably heated in a stream of hot nitrogen at a temperature up to 120 °C for a period of time sufficient to obtain a significant amount of branching.

WO 94/05707 discloses a process for the modification of linear or branched propylene (co)polymers containing not more than 5 % by weight of ethylene. Branching is introduced by reacting this resin at a temperature above 120 °C with a peroxide containing an activated unsaturated group. A particularly preferred peroxide is tert-butylperoxy-n-butylfumarate. The molecular weight of the modified resin may be influenced by the use of a coagent.

GB 1,566,056 discloses a process for the simultanous cross-linking, extrusion and foaming of branched polyolefins, in particular polypropylene and polybutene-1. The polyolefin mixed with a conventional peroxide is heated in an extruder for a period equal to at least one half of the half-life of the peroxide, then a liquefied gas acting as a foaming agent is

injected, the mixture is extruded through an extrusion die into ambient atmosphere to expand the extrudate.

US 5,082,869 relates to a foamed material obtained by feeding a not crosslinked polypropylene and a co-agent into a twin screw extruder wherein they are mixed and melted, and at a distance equal to 2/3 of the extruder length from the main inlet opening crosslinking and foaming agents are introduced into the molten material, which upon extrusion through a die expands into a foamed material having densities of 200 to 400 kg/m^3.

An object of the present invention is to provide a simple, continuous, commercially applicable process by which polypropylene resins can be branched and foamed into useful materials.

SUMMARY OF THE INVENTION

The present invention provides in a first aspect a process for the branching of a polypropylene resin being performed continuously in an extruder, comprising:

(i) mixing the polypropylene resin with a peroxide, and optionally also a crosslinking agent, which peroxide is selected from the group comprising the structures represented by the following formulae (1) and (2); and mixtures thereof:

$$R_1\text{-}O\text{-}O\text{-}C(O)\text{-}C{=}C\text{-}C(O)\text{-}O\text{-}O\text{-}R_2 \qquad (1)$$

$$R_3\text{-}R_5\text{-}O\text{-}C(O)\text{-}O\text{-}O\text{-}C(O)\text{-}O\text{-}R_6\text{-}R_4 \qquad (2)$$

wherein each R_1 and R_2, equal or different, represents alkyl groups having 1 to 15 carbon atoms, and which are branched or not, each R_3 and R_4, equal or different, represents alkyl groups having 4 to 30 carbon atoms, and which are branched or not, and each R_5 and R_6, equal or different, represents cyclic or linear aliphatic groups having 6 carbon atoms,

(ii) heating the constituents to a temperature higher than the melting temperature of the polypropylene resin and the decomposition temperature of the peroxide, while they are being mixed and conveyed forward,

(iii) keeping the polymer melt at said temperature for a period of at least 3 and until 100 times the half-life of the peroxide at said temperature, and

(iv) extruding the reacted polymer melt through an extrusion die into ambient atmosphere.

Further, the present invention also provides a process for the foaming of a polypropylene resin, being performed continuously in an extruder, comprising steps (i) to (iii) above and in addition the following steps:
(iv) introducing a foaming agent, optionally also a bubble initiator, into the polymer melt inside the extruder barrel at a position where the branching is substantially complete, and
(v) extruding the processed polymer melt through an extrusion die into ambient atmosphere, whereupon the polymer composition expands.

DETAILED DESCRIPTION OF THE INVENTION

The preferred polymer resins to be used in the present process are polypropylene resins. However, in principle any extrudable α-olefin polymer may be used. The term "polypropylene" or "polypropylene resins", as used herein, includes all types of propylene polymers, such as propylene homopolymers and copolymers, as well as blends and alloys containing polypropylenes as the major part. Particularly preferred polypropylenes are selected from the group comprising polypropylene homopolymers; copolymers of propylene with ethylene, containing from 0.1 to 25 % by weight of ethylene; blends of polypropylene with polyethylenes such as high density polyethylene (HDPE), low density polyethylene (LDPE), linear low density polyethylene (LLDPE); ethylene propylene rubbers (EPR); and alloys of polypropylene with another thermoplastic polymer selected from the group comprising polyamides (PA), polyethylene terephthalates (PET), polybutylene terephthalates (PBT), polycarbonates (PC) and polystyrenes (PS). Polypropylene blends or alloys may contain the second polymer component in an amount from 0.1 to 40 % by weight based on the weight of the polymer composition. The polypropylene, or main polypropylene component, should have a melt flow index from 0.2 to 500 g/10 min (determined at the conditions 230 °C/2.16 kg according to ASTM D 1238).

The peroxide employed in the present process shall induce chain branching of the polymer resin and thus broaden its molecular weight distribution (MWD). The peroxide must not cause any substantial amount of β-scissions in the polypropylene backbone, which inevitably will reduce the average molecular weight (Mw) of the polypropylene resin. The peroxide must decompose when exposed to a temperature range which is common in polypropylene extrusions. The half-life of the peroxide has to be shorter than the residence time of the melted resin in the extruder. Consequently, specific peroxides satisfying the above mentioned requirements have to be used.

Suitable peroxides can be selected from the group comprising those represented by the following formula (1):

$$R_1\text{-O-O-C(O)-C=C-C(O)-O-O-}R_2 \qquad (1)$$

wherein each R_1 and R_2, equal or different, represents alkyl groups having 1 to 15 carbon atoms, and which may be branched or not. Preferred peroxides of formula (1) are selected from the group comprising slightly branched alkyl fumarates. A particularly preferred peroxide is tert-butylperoxy-n-butylfumarate (TBPNBF), which has a half-life of about 6 minutes at 148 °C and about 30 seconds at 180 °C.

Peroxides can also be selected from the group comprising those represented by the following formula (2):

$$R_3\text{-}R_5\text{-O-C(O)-O-O-C(O)-O-}R_6\text{-}R_4 \qquad (2)$$

wherein each R_3 and R_4, equal or different, represents alkyl groups having 4 to 30 carbon atoms, and which may be branched or not; and each R_5 and R_6, equal or different, represents cyclic or linear aliphatic groups having 6 carbon atoms. Preferred peroxides of formula (2) are selected from the group comprising dialkyl peroxy dicarbonates. Particularly preferred peroxides are dicetyl peroxydicarbonates, dimyristyl peroxydicarbonate and similar peroxides having longer alkyl chain length. These peroxides have a half-life of about 1 second at 140 °C.

A preferred level of peroxide used by the present process is from 0.001 to 10 %, preferably from 0.1 to 5 %, more preferably from 0.5 to 2 %, based on the weight of the polypropylene resin.

Any mixture of the different peroxides having the general formulae (1) and (2) above may also be used.

The peroxides will upon heating decompose into free radicals which, by a certain reaction mechanism, will induce reactive sites on the polymer backbone, leading to the formation of branching. When using peroxides of the alkyl fumarate class (peroxides of formula (1)) the carbon-carbon double bond is expected to contribute to the mentioned mechanism and the resulting formation of branching by a "combination" of polyolefin chains. When using peroxides of the dialkyl peroxydicarbonate class (peroxides of formula (2)) the peroxides are believed being "grafted" onto the polyolefin chains, eventually leading to the formation of branching.

A crosslinking agent may also be added to the system to enhance branching. Suitable crosslinking agents comprise compounds having di- or triallyl groups and they may have either a cyclic or a linear aliphatic structure. Preferred crosslinking agents are selected from the group comprising tri(alkyl allyl)cyanurates and tri(alkyl allyl)isocyanurates. Particularly preferred crosslinking agents are triallyl cyanurate and triallyl isocyanurate. A preferred level of crosslinking agent used by the present process is from 0.01 to 10 %, preferably from 0.1 to 5 %, by weight based on the weight of the polypropylene resin. The crosslinking agent is expected to function as a junction between polymer chains, thus resulting in branching.

Neighbouring chains on separate polymer molecules may also combine and thereby crosslink the polymer. However, recombinations of polymeric species must not occur in such an extent that there will be a substantial degree of crosslinking between the chains resulting in a significantly impoverished processability.

The introduced changes in the molecular structure will change the rheological properties of the polymer. One way of expressing such changes is to perform rheological measurements in a rheometer and compare the obtained tan(G*=3) values for a modified and unmodified polymer. The property

$\tan(G^*=3)$, where $G^* = -(G')^2 + (G")^2$

is calculated from the storage and loss modules as a function of shear rate. The lower the value of $\tan(G^*)$, the higher is the extent of branching. Branching is believed to lead to an increased entanglement of the polymer chains, and this will increase the melt strength of the resin when being extruded. Consequently, a low $\tan(G^*)$ indicates a high melt strength.

Experiments show that the extrusion of a polypropylene mixed with a peroxide of formulae (1) and (2) above will result in a final resin having a reduced $\tan(G^*)$ value. In contrast, most of the peroxides commonly employed in plastic processing will increase the value of $\tan(G^*)$, which indicates that the polymer chains have been degradeded rather than branched. Therefore, it is critical to selected a suitable type of peroxide, and it is important that the free radicals formed do not cause degradation by β-scissions of the polymer backbone.

Another way of expressing such rheological changes is a direct measurement of the melt strength of the polymer by a so-called "haul-off" method. This method is common in thermoplastic testing. Therefore, only a brief summary of the method to give a necessary understanding of its principles will be given. The polymer to be tested is extruded through a capillary die vertically downward. The formed thread is pulled downward by a weight connected to a scale recording the pulling force. This method makes it possible to measure the melt strength of the polymer thread in a molten state just outside the capillary die. The extruded solidified thread is hauled off by the use of a pair of nip rollers. The measured melt strength will vary with the haul off speed. Details are given in the examples. A high "haul off" force indicates an improved melt strength.

The foaming agent may be any physcial or chemical foaming agent. Examples of physical blowing agents comprise: carbon dioxide (CO_2); various hydrocarbons, in particular alkanes having 1 to 8 carbon atoms, preferably methane, ethane, propane, butane, isobutane (2-methylpropane), pentane, isopentane (methylbutane) and neopentane (2,2-dimethylpropane), most

preferably isobutane and pentane; water (H_2O); chloro-fluoro-carbons (CFC); and mixtures thereof. Examples of chemical blowing agents comprise: inorganic carbonates, citric acid and azodicarbon amides, and mixtures thereof.

A bubble initiator can be employed to improve the foam structure. Such an initiator can be any solid that will initiate the formation of bubbles from an introduced gasous or gas precursor compound. Thus, a bubble initiator can be selected among inorganic compounds, such as talc, and organic compounds, such as azodicarbonamides and citric acid. An introduced chemical blowing agent can also itself function as a bubble initiator.

The density of the foamed polypropylene resin will depend on various factors. Important is the degree of entanglement of the polymer chains, i.e. the degree of branching and/or cross-linking. If a greater amount of peroxide is mixed in during extrusion, this will result in a desired lower foam density and reduced average bubble size. Moreover, the type and amount of foaming agent used will influence the foam structure. For example, CO_2 will normally result in a higher foam density and larger foam bubbles than what is achieved when using isobutane. By the present invention the foam density and average bubble size can be desirely varied by selecting appropriate processing parameters. A person skilled in the art having learned the principles of this invention will know after having performed some experimental runs how to obtain the desired foam density.

Common additives, such as fillers, pigments, stabilisers, flame retardants, may be added to the resins used in the present process. In general, such additives will normally not have any influence on the branching reactions. They may however enhance the polymer properties and foaming performance.

The process of obtaining branching and foaming according to the present invention is preferably performed in a continuous manner by the use of a suitable extruder. All ordinary, com-

mercially available single and double screw extruders suitable for polypropylene extrusions may be used. Depending on the type of peroxide used, a vented extruder may be required. In general, all constituents except the foaming agents, i.e. the polyolefin resin, the peroxide, any additives and sometimes also the crosslinking agent, may be fed to the extruder together or as separate streams to the same inlet opening. Most conveniently, all components are fed to the same hopper and mixed therein by means well known in the art. However, it may be necessary to premix the peroxide into the resin to be sure that it be evenly distributed in the resin. The foaming agent will normally be introduced into the extruder barrel at a point in a distance of between 10 D and 30 D downstream from the hopper (where D is the diameter of the extruder barrel).

The extruder will provide an intimate mixing of the peroxide with the resin while the resin being subjected to melting and heating to a desired temperature. The selected peroxide must decompose at an acceptable rate at this particular temperature. The temperatures in the polymer melt in the mixing and metering zones of the extruder are preferably within the range of 120 °C to 250 °C, more preferably from 130 °C to 230 °C, most preferred from 140 °C to 210 °C. Chosen temperatures will depend on the type of polypropylene resin used and the specific conditions selected for foaming. The residence time of the melted resin inside the extruder must be sufficient to ensure the completion of the branching reactions, as well as sufficient mixing and distribution of the foaming agent(s). Consequently, the residence times will be closely linked to the temperature of the polymer melt, the half-life temperature of the peroxide and the type of foaming agent(s) used. In general, the dwell time should not be shorter than 3 times the half-life of the peroxide used. When the residence times are longer than 100 times the half-life of the peroxide no further increase in branching will normally be observed. Preferably, the residence time of the polymer resin inside the extruder is from 2 to 50 times the half-life of the peroxide at the actual melt temperature.

The present process can be carried out in an ambient atmosphere, but none the less an inert atmosphere, e.g. a nitrogen atmosphere, inside the extruder is preferred because this favours the branching.

According to one embodiment of the invention, the branched polypropylene is extruded without any foaming agent be added. The melted material will normally be extruded for example as strands which in an expedient manner are cooled and granulated. The obtained resin granules may be used as such in common thermoplastic processing, such as injection molding, extrusion coating, pipe extrusion, thermoforming, blow molding, calandering, fibre spinning.

According to a preferred embodiment of the invention, a foaming agent is introduced into the extruder barrel at a position where at least a substantial part of the polymer material has been branched. Also in this case the polymer melt can be extruded at ambient conditions. The extrudate, for example strands, will then expand. The obtained foamed strands are cooled and may be granulated as mentioned above. The produced foamed resin granules (foamed beads) may be used as such in secondary plastic processing. Another option is to shape the foamed extrudate directly into desired foamed products, like monolayer or multilayer sheets, profiles, tubes, or other shapes. These semifinished foamed products may be used as such or in further plastic manufacturing, for example in thermoforming, lamination, or for other purposes.

The invention will now be illustrated and described in greater details by examples, which should not be construed as limiting the invention.

EXAMPLES

Determination of physical properties

Rheological properties were determined by the use of an oscillating rheometer, "Rheomterics RDA II" (trademark). The following test conditions were used: a capillary rheometer piston speed of 1 mm/min, a die geometry of 16:1, and a

temperature of 190°C. The melt strength was determined by comparing the measured tan(G^*=3) value of the sample with the corresponding value of a reference (unmodified) sample, as explained above.

Melt strength was determined by the above-mentioned "haul-off" method by using a capillary rheometer apparatus available under the trademark "Rosand RH07". The polymer sample was conditioned for 10 minutes before extrusion. The haul off speed of the solidified extruded monofilament ranged from 2 to 50 m/min. At a given speed a higher recorded force indicates a higher melt strength.

The foam density was determined by weighing a sample, measuring the displaced volume of the sample in a high accuracy measuring cylinder, and then divide the weight by volume. The average cell (bubble) sizes were determined by counting manually the number of cells on a Scanning Electron Microscopy (SEM) picture of the cross-section of an extruded strand.

Example 1

This example relates to the branching of a propylene/ethylene copolymer by the use of a peroxide of formula (1).

A random propylene-ethylene copolymer containing 2 % by weight of ethylene (polymer grade designated RD-1), having a melt index of MFI=8 (230 °C/2.16 kg, determined according to ASTM D 1238), was premixed with 1 % by weight of tert-butylperoxy-n-butylfumarate (TBPNBF), which has a half-life of 30 seconds at 180 °C. This premix was extruded in an ordinary twin screw extruder of type "Clextral BC 21" (trademark) having corotating intermeshing screws, a barrel diameter of D=25 mm and a screw length, L, equal to L/D=44. The set temperature profile resulted in a melt temperature at the sieve of approximately 180 °C. The screw speed was 150 rpm, resulting in a polymer resin dwell time of 8 times the half-life of the peroxide at 180 °C. The polymer melt was extruded as strands into a water bath, dried and comminuted into granules. Rheological measurements on the obtained resins, represented by tan(G^*=3), are reported in Table 1.

Example 2 (comparative example)

The procedure of example 1 was followed, except that 0.8 % by weight of tert.-butyl peroxybenzoate was added (commercially available from Akzo Nobel Chemicals bv under the trade name "Trigonox C"). (A concentration of 0.8 wt% Trigonox C corresponds to 1 wt% TBPNBF calculated on the basis of the active oxygen content). The measured tan(G^*=3) is reported in Table 1.

Example 3 (comparative example)

The procedure of example 1 was followed, except that no peroxide was used (control sample). The measured tan(G^*=3) is reported in Table 1.

Table 1

Resin RD-1, twin screw extruder

Ex. No.	Peroxide	Peroxide conc. (%wt)	tan(G^*=3)
1	TBPNBF	1	0.54
2 comp.	Trigonox C	0.8	1.7
3 comp.	none	0	1

Example 4 and Example 5 (comparative example)

The procedure of example 1 was repeated, except that a single screw extruder of type "Brabender" (trademark) having a diameter of D=30 mm and a length of L/D=26 was used The screw speed was 30 rpm, and the average melt temperature in the die zone was 180 °C. The residence time in the extruder was about 3 minutes. Example 4 was performed with the peroxide TBPNBF, and example 5 was performed without any peroxide. Rheological properties represented by tan(G^*=3) are reported in table 2.

Table 2

Resin RD-1, single screw extruder (D=30 mm)

Ex. No.	Peroxide	Peroxide conc. (%wt)	tan(G^*=3)
4	TBPNBF	1	0.27
5 comp.	none	0	1

Examples 6 to 8

These examples relates to the branching of a polypropylene homopolymer in a double screw extruder.

The procedure of example 1 was repeated, except that the polymer resin used was a polypropylene homopolymer (polymer grade designated HO-1) having a melt index of MFI=3. The peroxide levels used were as indicated in table 3 below. Determined rheological properties represented by tan(G^*=3) are reported in table 3.

Examples 9 and 10 (comparative example)

The procedure of examples 6 to 8 was followed, except that in example 9 was used 0.4 wt% of Triganox C and in example 10 no peroxide was used. Determined rheological properties represented by tan(G^*=3) are reported in table 3.

Table 3

Resin HO-1, twin screw extruder (D=25mm)

Ex. No.	Peroxide	Peroxide conc. (%wt)	tan(G^*=3)
6	TBPNBF	0.5	0.76
7	TBPNBF	1	0.58
8	TBPNBF	2	0.36
9 comp.	Triganox C	0.4	2.2
10 comp.	none	0	1

Example 11

This example relates to the branching of a polypropylene homopolymer by the use of a peroxide of formula (2) and cross-linking.

A propylene homopolymer (polymer grade designated HO-2) having a melt index of MFI=2 was premixed with 1.25 % by weight of dicetyl peroxydicarbonate (DCPDC), which has a half-life of about 1 second at 140 °C. This premix was extruded in the twin screw extruder used in example 1. The set temperature profile resulted in a melt temperature at the sieve of approximately 180 °C. The screw speed was 150 rpm, resulting in a polymer resin dwell time of 8 times the half-life of the peroxide at 180 °C. The polymer melt was extruded as strands into a water bath, dried and comminuted into granules. Rheological properties represented as melt strength measured by haul-off are reported in table 4.

Examples 12 to 14

The procedure of example 11 was repeated, except that in addition it was added from 0.1, 0,98 and 3.04 % by weight, respectively, of triallyl cyanurate (TAC) to act as a cross-linking agent. Rheological properties represented as melt strength measured the haul-off test method are reported in table 4.

Example 15 (comparative example)

Example 3 was repeated, except that no peroxide was added. Rheological properties represented as melt strength measured by haul-off are reported in table 4.

Table 4

Resin HO-2, twin screw extruder (D=25mm)

Ex. No.	Peroxide type	Peroxide %wt	Cross-linking agent type	Cross-linking agent %wt	Haul off force g
11	DCPDC	1.25	none	0	2.5
12	DCPDC	1.25	TAC	0.10	2.8
13	DCPDC	1.25	TAC	0.98	3.3
14	DCPDC	1.90	TAC	3.04	3.7
15 comp.	none	0	none	0	1.1

Example 16

This example relates to the branching and foaming of a polypropylene homopolymer.

The procedure of example 11 was followed, except that the concentration of dicetyl peroxydicarbonate (DCPDC) was 0.50 % by weight. In addition 5.0 % by weight of CO_2 as a foaming agent was introduced, and 1.0 % by weight of azodicarbonamide as a bubble initiator. The foaming agent was introduced into the extruder in a position located 18 D downstream of the first inlet point of the extruder. The foam density and foam average cell size were measured. The obtained results are reported in table 5.

Example 17

The procedure of Example 16 was repeated, except that the foaming agent used was isobutane. The results are reported in Table 5.

Example 18

The procedure of Example 17 was repeated, except that the amount of DCPDC was increased to 1.25 % by weight. The results are reported in Table 5.

Example 19 (comparative example)

Example 16 was repeated, except that no peroxide was added. The results are reported in table 5.

Table 5

Resin HO-2, twin screw extruder (D=25mm)

Ex. No.	Per-oxide	Per-oxide conc. (%wt)	Foaming agent	Foaming agent conc. (%wt)	Foam density (kg/m^3)	Average cell size (µm)
16	DCPDC	0.50	CO_2	5.0	175	125
17	DCPDC	0.50	iso-butane	5.0	150	90
18	DCPDC	1.25	iso-butane	5.0	90	65
19 comp.	none	0	CO_2	5.0	400	300

Claims

1. A process for the branching of a polypropylene resin, **characterised** by being performed continuously in an extruder, comprising:

(i) mixing the polypropylene resin with a peroxide and optionally also a crosslinking agent, which peroxide is selected from the group comprising the structures represented by the following formulae (1) and (2) or mixtures thereof:

$$R_1\text{-}O\text{-}O\text{-}C(O)\text{-}C{=}C\text{-}C(O)\text{-}O\text{-}O\text{-}R_2 \quad (1)$$

$$R_3\text{-}R_5\text{-}O\text{-}C(O)\text{-}O\text{-}O\text{-}C(O)\text{-}O\text{-}R_6\text{-}R_4 \quad (2)$$

wherein each R_1 and R_2, equal or different, represents linear or branched alkyl groups having 1 to 15 carbon atoms, each R_3 and R_4, equal or different, represents linear or branched alkyl groups having 4 to 30 carbon atoms, and each R_5 and R_6, equal or different, represents cyclic or linear aliphatic groups having 6 carbon atoms,

(ii) heating the constituents to a temperature higher than the melting temperature of the polypropylene resin and the decomposition temperature of the peroxide while being mixed and conveyed forward,

(iii) keeping the polymer melt at said temperature for a period of at least 3 and until 100 times the half-life of the peroxide at said temperature,

(iv) extruding the reacted polymer melt through an extrusion die into ambient atmosphere.

2. A process for the branching and foaming of a polypropylene resin, **characterised** by being performed continuously in an extruder, comprising:

(i) mixing the polypropylene resin with a peroxide and optionally also a crosslinking agent, which peroxide is selected from the group comprising the structures represented by the following formulae (1) and (2) or mixtures thereof:

$$R_1\text{-}O\text{-}O\text{-}C(O)\text{-}C{=}C\text{-}C(O)\text{-}O\text{-}O\text{-}R_2 \quad (1)$$

$$R_3\text{-}R_5\text{-}O\text{-}C(O)\text{-}O\text{-}O\text{-}C(O)\text{-}O\text{-}R_6\text{-}R_4 \quad (2)$$

wherein each R_1 and R_2, equal or different, represents linear or branched alkyl groups having 1 to 15 carbon atoms, each R_3 and R_4, equal or different, represents linear or branched alkyl

groups having 4 to 30 carbon atoms, and each R_5 and R_6, equal or different, represents cyclic or linear aliphatic groups having 6 carbon atoms,

(ii) heating the constituents to a temperature higher than the melting temperature of the polypropylene resin and the decomposition temperature of the peroxide while being mixed and conveyed forward,

(iii) keeping the polymer melt at said temperature for a period of at least 3 and until 100 times the half-life of the peroxide at said temperature,

(iv) introducing a foaming agent, optionally also a bubble initiator, into the polymer melt inside the extruder barrel at a position where the branching is substantially complete,

(v) extruding the processed polymer melt through an extrusion die into ambient atmosphere, whereupon the polymer composition expands.

3. The process of claims 1 or 2, **characterised** in that the polypropylene resin is selected from the group comprising polypropylene homopolymers; copolymers of propylene with 0.1 % to 25 % by weight of ethylene; blends of propylene homopolymers or copolymers with high density polyethylene, low density polyethylene, linear low density polyethylene or ethylene propylene rubbers; and alloys of propylene homopolymers and copolymers with other thermoplastic polymers selected from the group of polyamide and thermoplastic polyester resins; where the level of the second polymer in the blends or alloys is in the range of from 0.1 to 40 % by weight of the polymer composition.

4. The process of claims 1 or 2, **characterised** in that the residence time of the polymer resin inside the extruder is from 2 to 50 times the half-life of the peroxide at the actual melt temperature.

5. The process of claims 1, 2 or 3, **characterized** in that an amount of peroxide in the range of from 0.001 % to 10 % based on the weight of the polypropylene resin is used.

6. The process of any of claims 1 to 5, **characterised** in that the peroxide is selected from the group comprising tert-butyl-peroxy-n-butylfumarate, dicetyl peroxydicarbonates and dimyristyl peroxydicarbonate.

7. The process of any of claims 1 to 6, **characterised** in that the crosslinking agent is selected from the group comprising tri(alkyl allyl) cyanurates or tri(alkyl allyl) isocyanurates.

8. The process of claim 7, **characterised** in that the crosslinking agent is triallyl cyanurate or triallyl isocyanurate.

9. The process of claims 7 or 8, **characterized** in that an amount of crosslinking agent in the range of from 0.01 % to 10 % based on the weight of the polypropylene resin is used.

10. The process of claim 2, **characterised** in that the foaming agent is selected from the group comprising physical and chemical foaming agents, and mixtures thereof.

11. The process of claim 10, **characterised** in that the foaming agent is selected from the group comprising carbon dioxide, alkanes having 1 to 5 carbon atoms, nitrogen, water and chloro-fluorocarbons, and mixtures thereof.

12. The process of claim 11, **characterized** in that the foaming agent is CO_2 or isobutane.

13. The process of claims 2 to 12, **characterised** in that the bubble initiator is selected from the group comprising inorganic carbonates, citric acid and azodicarbon amides, and mixtures thereof.

14. A use of the polymer resins obtained by the process of any of claims 1 and 3 to 8, in manufacturing articles by injection molding, extrusion coating, pipe extrusion, thermoforming, blow molding, calandering and fibre spinning.

15. A use of the polymer resins obtained by the process of claims 2 to 13, in manufacturing articles by pipe extrusion, thermoforming and blow molding.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 99/00209

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C08F 8/00, C08L 23/26, C08J 9/04, B29C 44/50
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C08F, C08K, C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 9927007 A1 (AKZO NOBEL N.V.), 3 June 1999 (03.06.99), claims, abstract --	1-15
X	WO 9749759 A1 (AKZO NOBEL N.V.), 31 December 1997 (31.12.97), page 4, line 8 - line 23, page 5, line 13 - line 16, page 8, line 15 - line 21, page 9, line 8 - line 17, page 10, line 9 - line 22, claims 4-7, 15-18, 21-22 --	1-6,14-15
Y	WO 9405707 A1 (AKZO N.V.), 17 March 1994 (17.03.94), page 8, line 13 - line 33, page 10, line 7 - line 19, claims, abstract --	1-15

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 November 1999	23 -11- 1999
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Monika Bohlin/EÖ Telephone No. +46 8 782 25 00

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 99/00209

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5082869 A (VITTORIO BRAGA ET AL), 21 January 1992 (21.01.92), column 3, line 7 - line 16, column 4, line 9 - line 41	2-15
Y	US 5447985 A (ANTHONY J. DENICOLA, JR. ET AL), 5 Sept 1995 (05.09.95), column 2, line 12 - line 17, column 4, line 27 - line 55, column 5, line 45 - line 62, column 7, line 36 - line 41	1,3-9,14-15
Y	US 5416169 A (JUN SAITOET AL), 16 May 1995 (16.05.95), column 1, line 63 - line 66; column 2, line 9 - line 16; column 3, line 55 - column 5, line 29, column 6, line 67 - column 7, line 2, column 12, line 28 - line 33, column 12, line 63 - column 14, line 14	1-5,7-12, 14-15
Y	US 4916165 A (TAKASHI HASHIMOTO ET AL), 10 April 1990 (10.04.90), claims 1-3, 11 and 13	1-5,7-12, 14-15
A	GB 1566056 A (S. T. DUPONT), 30 April 1980 (30.04.80), claims	1-15
P,A	Journal of Applied Polymer Science, Volume 73, 1999, Masataka Sugimoto et al, "Effect of Chain Structure on the Melt Rheology of Modified Polypropylene" page 1493 - page 1500	1-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/11/99

International application No.
PCT/NO 99/00209

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9927007 A1	03/06/99	AU 1669399 A	15/06/99
WO 9749759 A1	31/12/97	AU 3258497 A	14/01/98
		CA 2258954 A	31/12/97
		EP 0907677 A	14/04/99
		NO 986102 A	23/12/98
		PL 330900 A	07/06/99
WO 9405707 A1	17/03/94	AT 142654 T	15/09/96
		DE 69304707 D,T	06/03/97
		EP 0656911 A,B	14/06/95
		SE 0656911 T3	
		ES 2092832 T	01/12/96
		JP 8504842 T	28/05/96
		US 5464907 A	07/11/95
US 5082869 A	21/01/92	CA 2037956 A	10/09/91
		DE 69113665 D,T	02/05/96
		EP 0450342 A,B	09/10/91
		ES 2078367 T	16/12/95
		IT 1242305 B	04/03/94
		IT 4100490 D	00/00/00
		JP 6200100 A	19/07/94
US 5447985 A	05/09/95	AT 182346 T	15/08/99
		CA 2175207 A	04/05/95
		DE 69419618 D	00/00/00
		EP 0728159 A,B	28/08/96
		JP 10502391 T	03/03/98
		WO 9511938 A	04/05/95
US 5416169 A	16/05/95	DE 4340194 A	01/06/94
		JP 2869606 B	10/03/99
		JP 6157666 A	07/06/94
		JP 2814337 B	22/10/98
		JP 6263823 A	20/09/94
		JP 2844290 B	06/01/99
		JP 6299013 A	25/10/94
US 4916165 A	10/04/90	CA 1269494 A	22/05/90
		DE 3681300 A	17/10/91
		EP 0190021 A,B	06/08/86
		JP 1813061 C	27/12/93
		JP 5024930 B	09/04/93
		JP 61171742 A	02/08/86
		US 4870114 A	26/09/89
		JP 1813062 C	27/12/93
		JP 5024931 B	09/04/93
		JP 61176636 A	08/08/86
		JP 1813064 C	27/12/93
		JP 5024932 B	09/04/93
		JP 61181841 A	14/08/86
		JP 1847443 C	07/06/94
		JP 5062617 B	08/09/93
		JP 61185533 A	19/08/86

INTERNATIONAL SEARCH REPORT

Information on patent family members

02/11/99

International application No.
PCT/NO 99/00209

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 1566056 A	30/04/80	BE 851850 A	25/08/77
		DE 2707874 A	01/09/77
		FR 2342148 A,B	23/09/77
		IT 1071581 B	10/04/85
		NL 7702105 A	30/08/77

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